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**14. ABSTRACT**

The focus of this proposal is to develop biotechnological approaches for the synthesis of efficient dye sensitizers and redox polyelectrolytes in an environmentally benign way using enzymatic or biomimetic techniques. To further develop processing techniques to fabricate photovoltaic cells on thin conformable substrates and to test the dyes and polyelectrolytes thus prepared in realistic device configurations and establish close collaboration with a company to transition the results of the research.

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## **Biotechnology Route to Conformal Photovoltaics**

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### **LONG-TERM GOALS**

To develop a biotechnology route for the fabrication of nanocrystalline  $\text{TiO}_2$  based dye-sensitized photovoltaic (DSPV) cells on conformable substrates.

### **OBJECTIVES**

1. To develop biotechnological approaches for the synthesis of efficient dye sensitizers and redox polyelectrolytes in an environmentally benign way.
2. To develop processing techniques to fabricate photovoltaic cells on thin conformable substrates.
3. To test the dyes and polyelectrolytes thus prepared in realistic device configurations throughout the project.

### **APPROACH**

#### *Year 2001*

1. Enzymatically synthesize pyrene-based macrodyes in water/solvent mixtures.
2. Monitor, in situ, the peroxidase-catalyzed polymerization of 1-hydroxypyrene by UV-Vis and fluorescence spectroscopy.
3. Investigate the structure of the synthesized poly(1-hydroxypyrene) by NMR and FTIR spectroscopy.

#### *Year 2002*

1. Synthesis of a Phenolic ligand, 4-([1,10] Phenanthroline-5-yliminomethyl)-phenol (APHB).
2. Hematin catalyzed polymerization of APHB in dimethylformamide (DMF).
3. Complexation of above polymer (PolyAPHB) with Ruthenium complex,  $\text{Ru}[(\text{bpy})_2\text{Cl}_2]$  to obtain a Macromolecular complex,  $\text{Ru}[(\text{bpy})_2(\text{APHB})]_n$  (PolyRuAPHB).
4. Characterization of monomer and polymer by UV-Vis, FTIR, NMR, Fluorescence spectroscopy.

5. Photovoltaic measurements on PolyRuAPHB as a sensitizer in TiO<sub>2</sub> based solar cells.

#### Year 2003

1. Hematin catalyzed synthesis of a planar and conjugated bridging ligand (tpphz)
2. Synthesis of a dinuclear ruthenium complex (Ru\_tpbp) with tpphz as bridging ligand and dicarboxylic bipyridyl ligands. Photophysical and photovoltaic measurements on Ru\_tpbp in DSSCs.
3. Novozyme-435 catalyzed synthesis of novel pegylated polyelectrolyte systems
4. Photovoltaic measurements on TiO<sub>2</sub> based plastic DSSCs fabricated using above polyelectrolytes.

### **WORK COMPLETED**

Year 2001: Pyrene-based macromolecular dyes have been enzymatically synthesized. The properties and structures of the synthesized macromolecular dyes were characterized by UV-Vis, fluorescence, FTIR and NMR spectroscopy.

Year 2002: Synthesis of a 5- aminophenanthroline based phenolic ligand and its biocatalytic polymerization with Hematin have been carried out. A Ruthenium macromolecular complex using the poly ligand has been prepared. The structures of the synthesized macromolecular dye and monomer were characterized by UV-Vis, fluorescence, FTIR and NMR spectroscopy. The photophysical and photovoltaic properties of the macro dye were investigated.

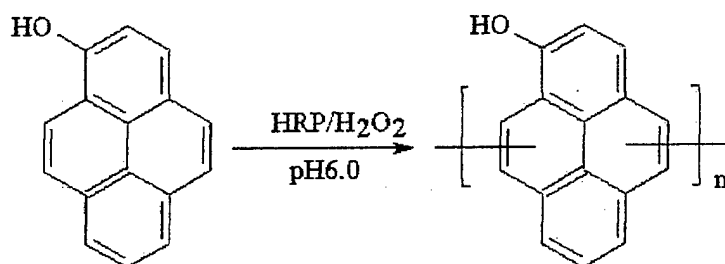
Year 2001: The biocatalytic synthesis of a planar, aromatic and fully conjugated bridging ligand, tetrapyrido[3,2-a:2',3'-c:3'',2''-h:2''',3'''-j]phenazine (tpphz) and a dinuclear Ruthenium complex using Hematin as a biocatalyst have been carried out for the first time. This recently developed bridging ligand is a very interesting system due to its favourable structural features. A ruthenium dinuclear complex with bipyridyl ligands has been synthesized using tpphz as bridging ligand and its photovoltaic properties in TiO<sub>2</sub> solar cells were measured. A polyethylene glycol (PEG) based polyester has been synthesized using Novozyme-435 as a biocatalyst and photovoltaic properties have been measured in TiO<sub>2</sub> solar cells on flexible substrates.

### **RESULTS**

#### Year 2001

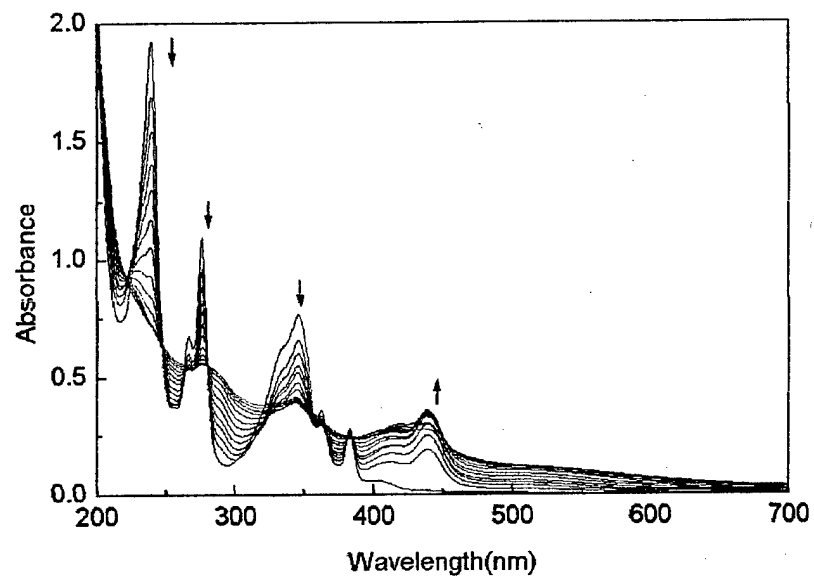
1-Hydroxypyrene was enzymatically polymerized in a mixture of 50% ethanol and 5% process of the reaction was monitored *in situ* by UV-Vis and fluorescence spectroscopy. The monomer, 1-hydroxypyrene, shows three major absorption peaks in the mixture of 0% buffer (0.01M phosphate) at pH 6.0 at room temperature as shown in Scheme 1. The

Scheme 1

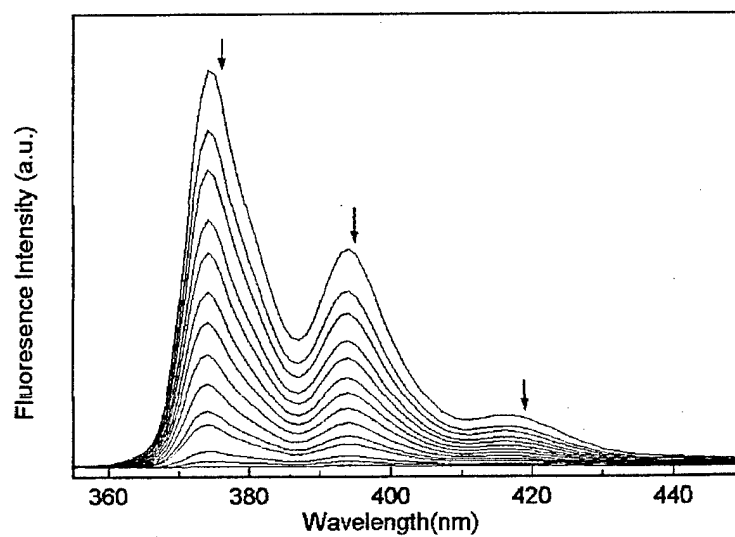


ethanol/water at 374, 394 and 416 nm, respectively (Figure 1).  $\text{H}_2\text{O}_2$  was added to initiate and facilitate the reaction. The major absorption peaks from the monomer decreased gradually, and a new absorption peak at approximately 450 nm emerged. This peak gradually increased with a tail absorption extended to longer wavelength, indicating that the final product has a longer conjugation length. The fluorescence spectrum of 1-hydroxypyrene, monomer gives three emission peaks at 374, 393 and 424 nm, respectively (Figure 2). Following with what was observed in the UV-Vis spectra, the fluorescence intensity decreases gradually as the reaction proceeds. After an equal molar amount of  $\text{H}_2\text{O}_2$  (relative to monomer) was added to the solutions, the fluorescence of the monomer was totally quenched, indicating total conversion of the monomer.

Similar reaction conditions as described above were used in the bulk synthesis of the poly(1-hydroxypyrene). 1-Hydroxypyrene is very active in this HRP-catalyzed oxidation reaction. With the progress of the reaction, the products were formed as powdery precipitates. The synthesized products were isolated by centrifugation, purified by washing with a mixture of ethanol and water (30% ethanol and 70% water). A brown-yellow powder was obtained after the precipitates were dried. The isolated yield of the reaction was ~80%. The powder was slightly dissolved in dioxane and DMF.

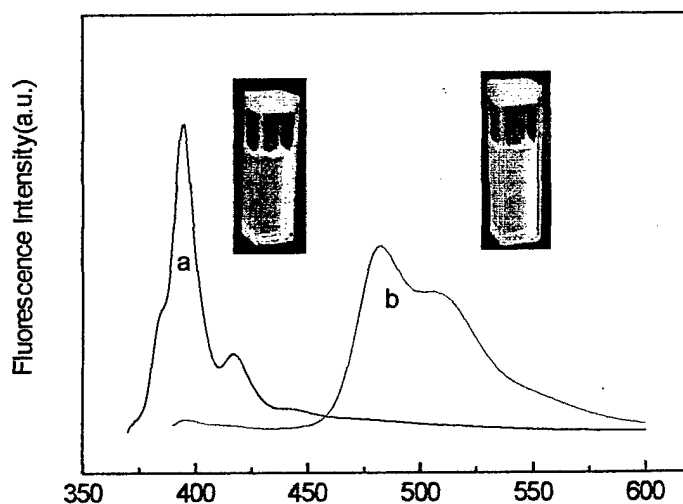


**Figure 1.** Evolution of UV-Vis spectra of HRP-catalyzed oxidation of 1-hydroxypyrene.



**Figure 2.** Evolution of fluorescence spectra of HRP-catalyzed oxidation of 1-hydroxypyrene. The excitation used was 355 nm.

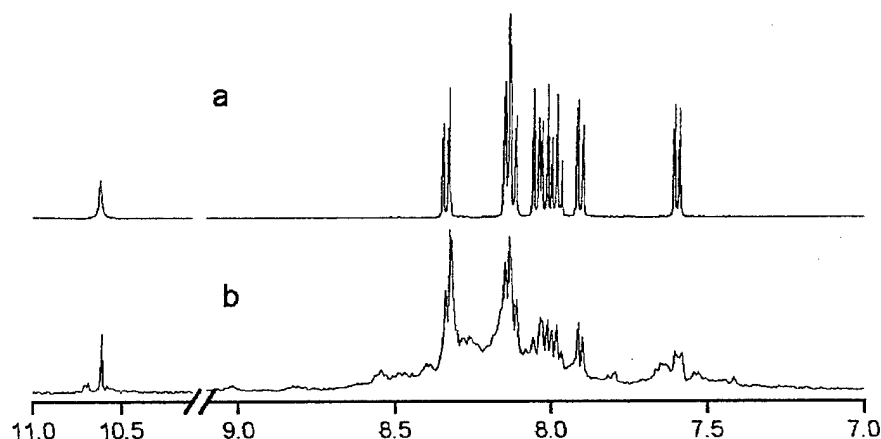
The synthesized poly(1-hydroxypyrene) didn't show any fluorescence emission in the mixture of ethanol and water during the reaction as was mentioned above. However, the synthesized products do emit strong fluorescence in anhydrous solvents, such as



**Figure 3.** The fluorescence spectra of the monomer (a) and synthesized products (b) in pure dioxane. The excitation wavelength used was 355m. The insets show the photos of the quartz cells that contain monomer and polymer solution pumped by a 360nm UV lamp.

ethanol, dioxane, and DMF, etc. The reason we don't see the fluorescence emission of the synthesized product during the reaction is due to the presence of water in reaction system. The fluorescence spectra of monomer and polymer of 1-hydroxypyrene in anhydrous dioxane are shown in Figure 3. The monomer of 1-hydroxypyrene shows a strong fluorescence peak at 394 nm in anhydrous dioxane with a shoulder at 416 nm. However, the peaks of the polymer fluorescence spectrum shift significantly to longer wavelength with a maximum emission peak at 482 nm and a shoulder at 509 nm. A red shift of ~70nm for the major peak of the polymer was observed compared to that of the monomer. The photos of the quartz cells containing the monomer and polymer solutions after excitation by a 360 nm UV lamp are shown as insets in Figure 3. Typically, the solution of the monomer in dioxane shows a purple-blue light emission, and the solution of the synthesized product in dioxane gives a blue-green light emission. It is known that pyrene derivatives will aggregate at high concentration to form excimer, which usually causes a red shift of the emission. In this case, the significant red shift of the emission of the synthesized products is not due to the formation of the excimer, since only low concentrations of monomer and polymer have been used in these measurements. The observed dramatic red shift of emission compared to the monomer may be explained by the increase of the conjugation length as observed in the UV-Vis absorption spectrum.

It has been reported previously that the structures of enzymatically synthesized polyphenols are very complicated due to the presence of the coupling of both C-C (two carbons on different aromatic rings coupled together, usually at the ortho position) and C-O-C (the oxygen from the hydroxy group on one aromatic ring coupled with the carbon on another aromatic ring) in the reaction. The main chain of the synthesized polyphenols is usually a mixture of phenylene and oxyphenylene units. The structure of the enzymatically synthesized pyrene product was characterized by  $^1\text{H}$  NMR (Figure 4) and FTIR spectroscopy in the present work. The results show similar structural features as that observed in the enzymatically synthesized polyphenols with both C-C and C-O-C coupling possibly being involved in the reactions. As one can see from the molecular structure of 1-hydroxypyrene, several radical resonance structures may be formed. Thus,



**Figure 4.**  $^1\text{H}$  NMR of 1-hydroxypyrene monomer (a) and polymer (b).

even more positions on the pyrene ring are available for coupling compared to that of the phenol. Thus the structure of the enzymatically oxidized 1-hydroxypyrene may be even more complicated compared to the polyphenols.

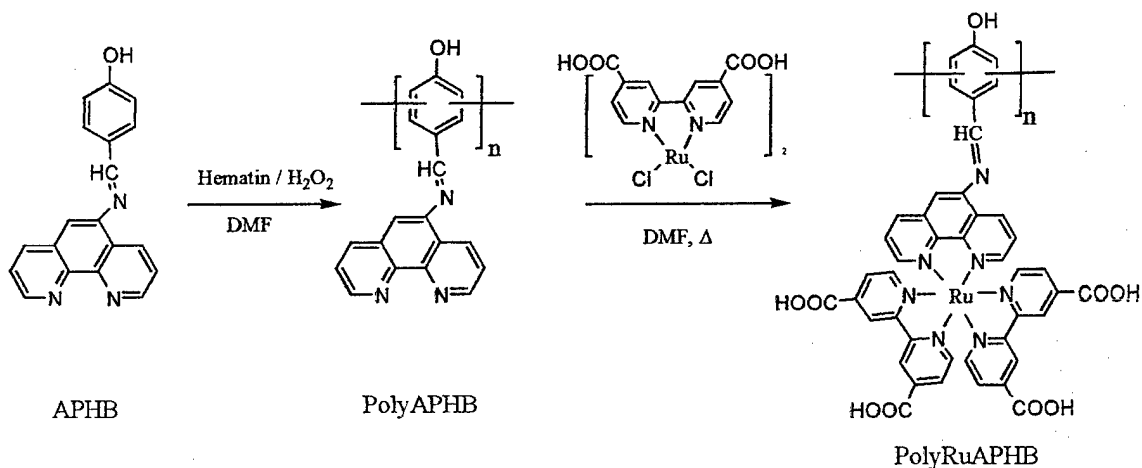
#### Year 2002

Synthesis of the phenolic ligand, 4-([1,10]Phenanthroline-5-yliminomethyl)-phenol (APHB) was carried out as follows. To a warm solution of 0.1g of 5-amino-1,10-phenanthroline in 25 ml of methanol, 0.062g of 4-hydroxybenzaldehyde dissolved in 5ml of methanol was added drop wise under  $\text{N}_2$  atmosphere. The reactants were heated to reflux for 5 hours and cooled to room temperature. The precipitate obtained was filtered and washed several times with methanol to obtain 0.12g of a yellow solid, 4-([1,10]Phenanthroline-5-yliminomethyl)-phenol (APHB). The product was recrystallized from N, N-dimethylformamide / ether. FTIR (KBr pellet):  $3428\text{ cm}^{-1}$  (OH stretching),  $3070\text{ cm}^{-1}$  (aliphatic C-H),  $1601, 1576\text{ cm}^{-1}$  (C=C stretching), UV-vis absorption:  $\lambda_{\text{max}}$  at

340 nm in ethanol solution;  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-d}_6$ )  $\delta$  10.3 (s, 1H),  $\delta$  9.1 (d, 1H),  $\delta$  9.0 (d, 1H),  $\delta$  8.8 (d, 1H),  $\delta$  8.7 (s, 1H),  $\delta$  8.4 (d, 1H),  $\delta$  7.9 (d, 2H),  $\delta$  7.7 (m, 2H),  $\delta$  7.6 (s, 1H),  $\delta$  6.9 (d, 2H).

The synthesis of the macrodye PolyRuAPHB was accomplished in two steps; Hematin catalyzed polymerization of APHB followed by the complexation as shown in Scheme 1. The ligand, APHB (0.02g) was dissolved in 5 ml of DMF by sonication. To this solution was added a catalytic amount (4 mg) of Hematin followed by drop wise addition of 30%  $\text{H}_2\text{O}_2$  (3 ml). The solution turned red on addition of the peroxide accompanied with vigorous evolution of oxygen. The reaction was allowed to proceed till completion and the solvent evaporated off under high vacuum. Repeated washings with ice-cold water-methanol were carried out to remove the traces of DMF and the dark colored solid obtained was recrystallized with acetone to yield 0.01g of the pure polymer, PolyAPHB. FT-IR (KBr):  $3428\text{ cm}^{-1}$  (OH stretching),  $2943\text{ cm}^{-1}$  (aliphatic C-H),  $1663\text{ cm}^{-1}$  (C=C stretching), UV-vis absorption (DMF solution):  $\lambda_{\text{max}}$  at 340 nm and a new peak appeared at 526 nm.  $^1\text{H}$  NMR: broad and featureless from 7-9 ppm.

**Scheme 1**



The polyAPHB (0.01g) obtained was dissolved in 5 ml of DMF and further complexation was carried out by adding 0.01g of  $\text{RuCl}_2\text{bpy}_2$  dissolved in 5 ml of DMF followed by refluxing the solution overnight. A dark colored precipitate (0.014g) obtained was filtered off and washed several times with acetone and methanol. The polymer, PolyRuAPHB was characterized by UV-vis, FTIR and  $^1\text{H}$  NMR spectroscopy. FT-IR (KBr pellet):  $3428\text{ cm}^{-1}$  (OH stretching),  $2943\text{ cm}^{-1}$  (aliphatic C-H),  $1701\text{ cm}^{-1}$  (C=O stretching),  $1614\text{ cm}^{-1}$  (C=C stretching); UV-vis absorption:  $\lambda_{\text{max}}$  at 340 nm in ethanol solution;  $^1\text{H}$  NMR: broad and featureless from 7-9 ppm.

The Hematin-catalyzed polymerization of 4-ethylphenol in a buffer solution of pH 11.0 has been earlier reported by Akkara *et al.* It was proposed that the iron group in Hematin interacted with hydrogen peroxide, resulting in changes in the oxidation state of iron, and which subsequently reacts with the substrate in a one-electron transfer reaction to produce the substrate radical and a new iron-heme complex. These substrate radicals consequently couple to form the polymer. There has also been another report on Hematin catalyzed vinyl polymerizations in aqueous media by Singh *et al.*, however only low molecular weight polymers were obtained with the former compared to HRP.

We have tried to explore the possibility of polymerization of the aforementioned monomeric ligand both in aqueous media as well as organic media using HRP and Hematin, respectively. No polymerization was observed in the case of HRP in aqueous media, which led us to investigate Hematin as an additional option. Hematin was found to be catalytically active in organic solvents and could efficiently catalyze the polymerization in dimethylformamide. Thus, in the present study we have carried out the polymerization of APHB in organic media in order to gain improved yields over a short period of time.

The monomer and the polymers were first characterized by FTIR spectroscopy. Figure 1 shows the combined FT-IR spectra of the monomeric ligand (APHB), polyligand (PolyAPHB) as well as the polymeric ruthenium complex (PolyRuAPHB). The Hematin catalyzed polymerization of phenolic compounds has been observed in previous reports to usually produce mixture of polymers with complicated structures similar to peroxidase-catalyzed polymers.

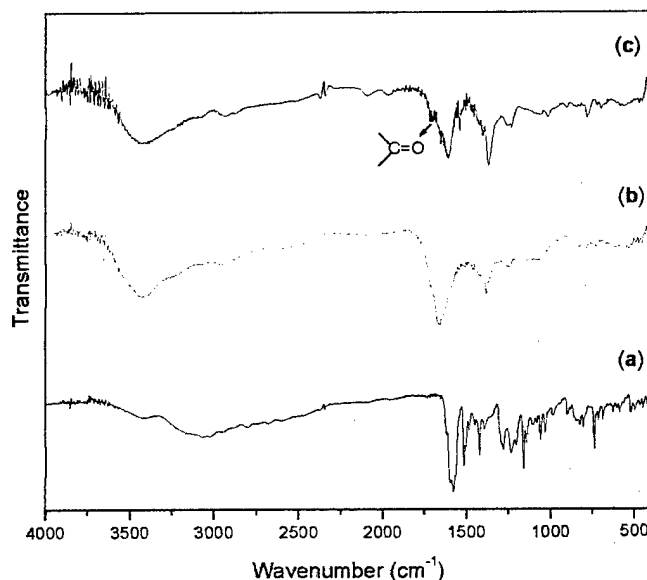
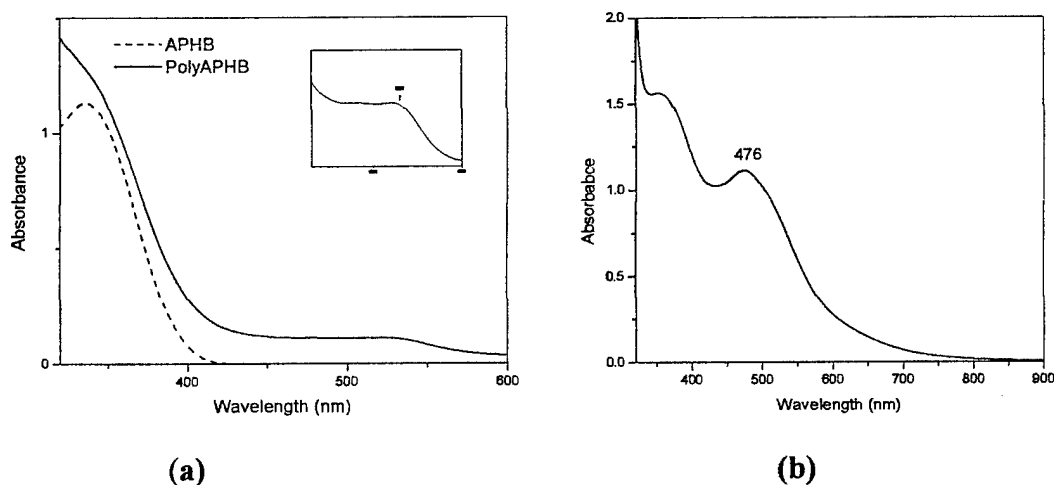


Figure 1. FT-IR spectrum of (a) APHB, (b) PolyAPHB and (c) PolyRuAPHB

Analogous to the macrodyes synthesized using HRP, the FTIR spectra of the polymer, PolyAPHB shows broad peaks around 3300-3000  $\text{cm}^{-1}$  attributed to the OH stretching and internal hydrogen bonding. The retention of a strong OH stretch region in the polymer suggests that most of the OH groups in the monomer are not involved in the coupling reaction and that the resulting polymer has significant phenol functionality. Due to the presence of the *para* substituted group at the phenyl ring, the vibrational stretching frequency ranging from 1700-600  $\text{cm}^{-1}$  is more broadened and thus complicated to analyze. The spectra of PolyRuAPHB shows a weak peak at 1701  $\text{cm}^{-1}$  due to carbonyl of carboxylic acid groups that are present on the bipyridyl ligand.

The  $^1\text{H}$  NMR spectra of the monomers show very sharp peaks compared to the broad peaks present in the spectrum of the polymer. This broadening of the proton NMR resonance peaks is attributed to polymerization and has been previously observed with numerous other enzymatically prepared polyphenol systems. The  $^1\text{H}$  NMR spectra of the PolyAPHB and PolyRuAPHB are essentially featureless with a broad peak ranging from 7 ppm to 9 ppm assigned to the aromatic protons. This unusual broadening can be attributed to either the high molecular weight or the broad distribution of the resulting polymers. However, the evident disappearance of *ortho* protons on the phenol ring implied that the most favored coupling takes place at *ortho* positions of the phenol ring in catalytic polymerization.

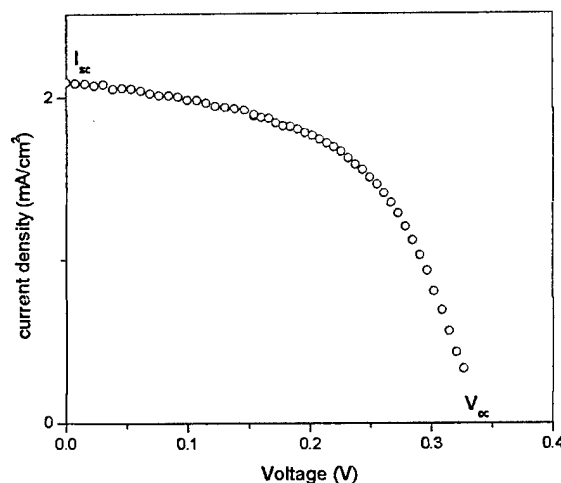


**Figure 2.** (a) UV-visible spectra of APHB and PolyAPHB (Inset shows magnified 420-600 nm region); (b) PolyRuAPHB measured in DMF solution.

Figure 2a shows an evaluation of the UV-visible absorption spectra of the monomeric ligand (APHB) and polymer (PolyAPHB). The spectrum of the ligand APHB exhibited absorption maxima at 340 nm which was retained in the polymer also. However, a weak and broad peak from 450-575 nm was also observed in the PolyAPHB spectrum which was attributed to the increase in conjugation due to coupling between aromatic rings. The spectra of the polymeric complex (PolyRuAPHB) is shown in Figure 2b. The peak at 476 nm is due to the metal-to-ligand charge transfer (MLCT) band and

the peak at 350 nm was assigned to the  $\pi-\pi^*$  transition within the ligands (5-amino-1, 10-phenanthroline and 4,4'-dicarboxylic bipyridyl ligands). This MLCT absorption band in polyRuAPHB suggests that the incorporation of the Ruthenium in the Polyligand (PolyAPHB) was successful. It is interesting to note that the absorption of cutoff wavelength is extended to 800 nm in the macrodye. This is an encouraging result from the point of view of exploiting efficient light harvesting properties in the near-IR region. The fluorescence measurements on monomeric complex and the final polymeric complex PolyRuAPHB were carried out. As typically expected, the polymerization of fluorescent chromophores resulted in decreased fluorescence due to increased local concentration quenching effect.

The DSPV cells were fabricated according to reported procedure using a liquid electrolyte (1.0 M LiI and 0.1M I<sub>2</sub> in acetonitrile) and exposed to simulated AM1.5 solar light at 1 sun of 100 mW/cm<sup>2</sup> light intensity using an Oriel 1000-W xenon lamp and appropriate filters. Photocurrents and photovoltages were measured using a Keithley 2400 source meter in conjunction with a personal computer. The current-voltage (I-V) curve measured for PolyRuAPHB is shown in Figure 3. The short circuit current density (I<sub>sc</sub>), open circuit voltage (V<sub>oc</sub>), fill factor (FF) and overall efficiency ( $\eta_e$ ) measured for this dye were found to be 2.1 mA/cm<sup>2</sup>, 340 mV, 0.48, 0.33% respectively in comparison to the efficiency of 3% that is observed for a standard dye, N3.



**Figure 3.** Current-voltage (I-V) curve measured for PolyRuAPHB sensitized DSPV cell.

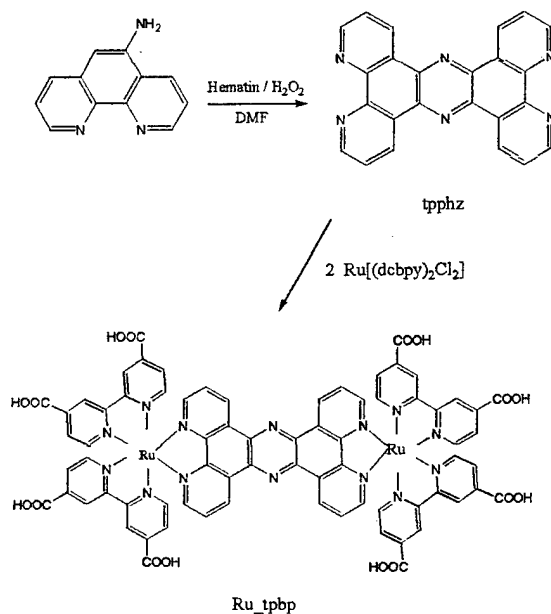
Year 2003

The single step biocatalytic method is very simple and proceeds under mild and environmentally friendly conditions compared to the reported multi step chemical methods. The synthesis of tpphz is carried out as follows (Scheme 1), where, 0.2g of 5-amino-1,10-phenanthroline (ap) and 3mg of Hematin were dissolved in 5 ml of N,N'-

dimethyl formamide (DMF) at room temperature and 0.1ml of 30% H<sub>2</sub>O<sub>2</sub> was added dropwise to initiate the reaction. The reaction was monitored by UV-Vis absorption spectroscopy. After stirring for 24 hrs, the pale yellow precipitate formed was filtered and washed with methanol and diethyl ether and purified by recrystallization from chloroform. Yield = 0.1g (25%). <sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>): 9.67 (dd, 4H), 9.39 (dd, 4H), 7.90 (dd, 4H). EI-MS (m/z): 384 (100).

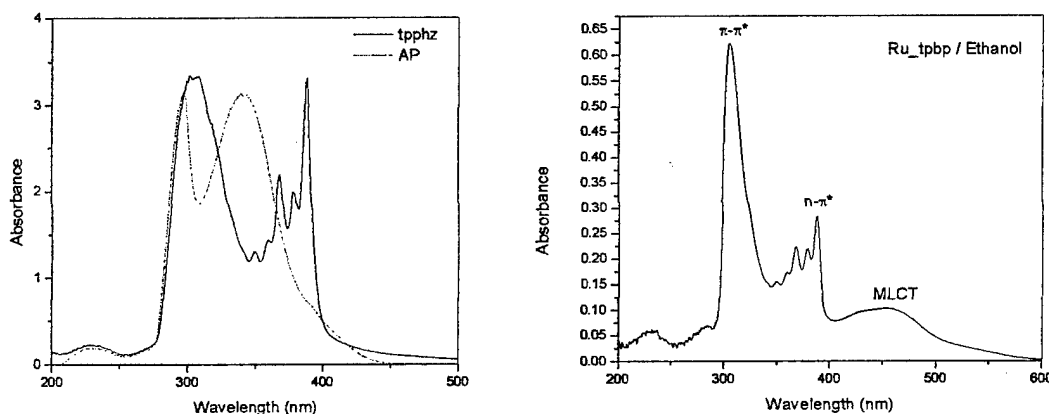
The biocatalytically synthesized tpphz was used to prepare the dinuclear complex, (Ru\_tpbp, Scheme 1) where dcbpy=4,4'-dicarboxylic bipyridyl. The ruthenium complex, [Ru(II)(dcbpy)<sub>2</sub>Cl<sub>2</sub>] was first synthesized following the reported procedure. To the tpphz solution in DMF added [Ru(II)(dcbpy)<sub>2</sub>Cl<sub>2</sub>] in 1:2 molar ratio and refluxed for 5 hours under N<sub>2</sub> atmosphere. The resultant precipitate was filtered and washed several times with acetone and ether. CHN Analysis calculated for [(dcbpy)<sub>2</sub>Ru(II)(tpphz)Ru(II)(dcbpy)<sub>2</sub>] 2Cl· 2H<sub>2</sub>O: C, 54.51; H, 3.50; N, 13.09. Found: C, 55.04; H, 3.05; N, 13.05.

**Scheme 1**



The UV-Visible absorption spectra of the starting compound, ap and tpphz, measured in DMF solution, are shown in Figure 1a. The sharp peaks observed at 388, 378, 368 nm are due to  $n-\pi^*$  transitions and a peak at 308 nm is attributed the  $\pi-\pi^*$  transitions. These spectra are consistent with earlier reports on tpphz. The UV-Visible absorption spectra of the dinuclear complex, Ru\_tpbp measured in ethanol solution is shown in Figure 1b. The sharp peaks observed at 388, 378, 368 nm are due to  $n-\pi^*$  transitions from tpphz ligand and an intense peak at 305 nm is attributed the  $\pi-\pi^*$  transitions in bipyridyl ligand. The broad peak observed at longer wavelength (458 nm)

is characteristic of metal-to-ligand charge transfer (MLCT) band. Photovoltaic properties

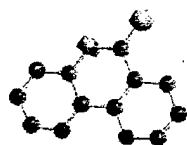


**Figure 1.** UV-Vis absorption spectra of (a) tpphz and (b) Ru\_tpbp

of Ru\_tpbp were measured in TiO<sub>2</sub> based dye-sensitized solar cells using AM1.5 simulated solar light on glass substrates. This dinuclear complex showed promising overall conversion efficiency of 2.1% (compared to N3 of 4.7%) and 7.1 mA/cm<sup>2</sup>, 0.54V, 0.56 as short circuit current density, open circuit voltage, fill factors respectively.

The earlier chemical methods to prepare tpphz, used either high reaction temperature (180°C) or multistep synthesis. One of the most attractive features of our biocatalytic method is the extremely simple synthetic protocol involved. The reaction is a single step and can be carried out under extremely mild and environmentally friendly conditions at room temperature. The advantage of this synthesis is that there were no other side products observed in the precipitate that was formed from the reaction solvent. The synthesis of dinuclear complex, Ru\_tpbp using this biocatalytic method is novel and can be explored further.

Spin density calculations which was performed using AM1, a semiempirical computational method on ap to investigate the reaction sites strongly support our observation. The amino nitrogen and the adjacent carbon radicals have high spin density values (C, 0.53; N, 0.80) as shown by yellow color spheres on these atoms in Figure 2..



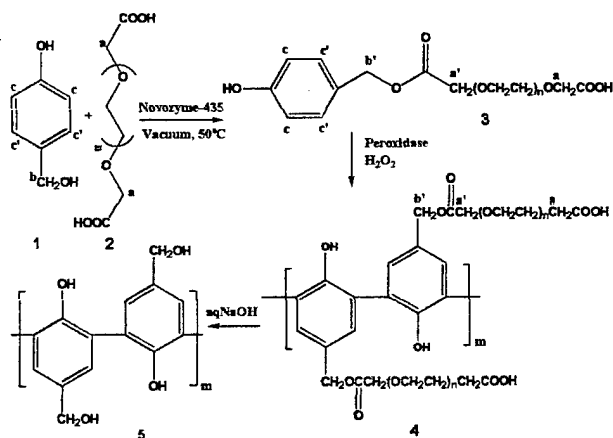
**Figure 2.** Calculated spin density (yellow spheres) on ap molecular radical.

This indicates that the reactivity of these two atoms is high for the formation of the dimer, tpphz. There could be an intermediate state where another hydrogen on the amino group is removed in the biocatalytic reaction to facilitate the formation of a stable aromatic system, tpphz.

The well-studied iodide/triiodide redox systems are used as a redox shuttle. We have focused our efforts on the development of readily processable polyelectrolytes that have high ionic conductivity and stability.

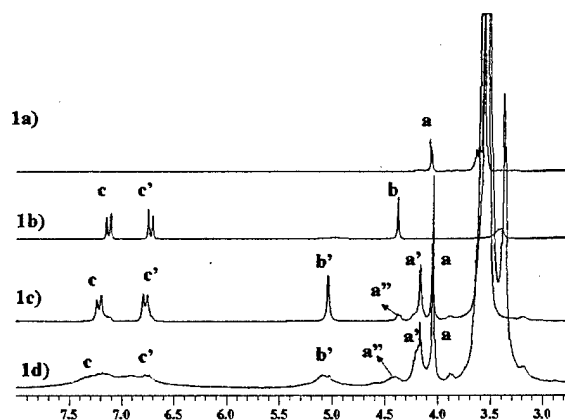
We utilized an enzyme to catalyze the highly chemoselective mono-acylation of the alcoholic hydroxyl group of 4-hydroxymethylphenol (**1**) with polyethylene glycol diacid (**2**) under solvent-less conditions. The free phenolic moiety of pegylated hydroxymethylphenol, **3** is then a substrate of peroxidase for the formation of the pegylated poly(hydroxymethyl phenol), **4**. The entire process (depicted in Scheme 2) does not require use of any organic solvents during the reaction and was performed either in solventless conditions or using water as a solvent, thus can be termed as a "Green process".

**Scheme 2**



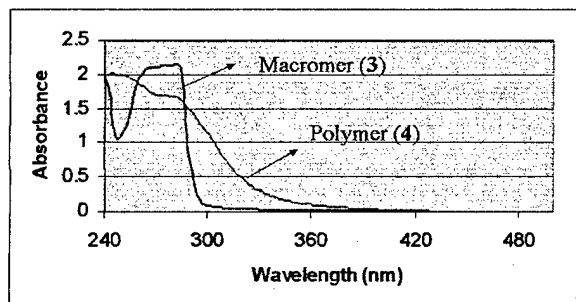
Polymerization of **3** was catalyzed separately by peroxidase from horseradish (HRP) in aqueous buffer over a wide range of pH values and resulted in water-soluble polymers with  $M_n$ 's ranging from 2000 to 15000 (degree of polymerization upto 20 with polydispersities of 1.4-1.8, determined by Gel Permeation Chromatography). HRP gave optimal molecular weight of pegylated polyphenolic, **4** at pH 4.5-6.0 with isolated yields of ca. 80% following dialysis to recover the polymer. The pegylated polyphenolic **4**, was fully characterized by its <sup>1</sup>H NMR (Figure 3 (1d)), <sup>13</sup>C NMR, UV (Figure 4) and IR spectroscopy. The <sup>1</sup>H NMR spectrum of polymer showed the presence of a broad signal in the range of  $\delta$  3.3-3.6 for the polyethylene glycol moieties and the signal at  $\delta$  5.2 corresponding to methylene proton labeled as b' in Figure 3(1d), further confirming that

the peg was attached to the polyphenol. The polymeric molecular weights obtained from this enzymatic polymerization reaction were highly dependent on the pH of buffer solution. It



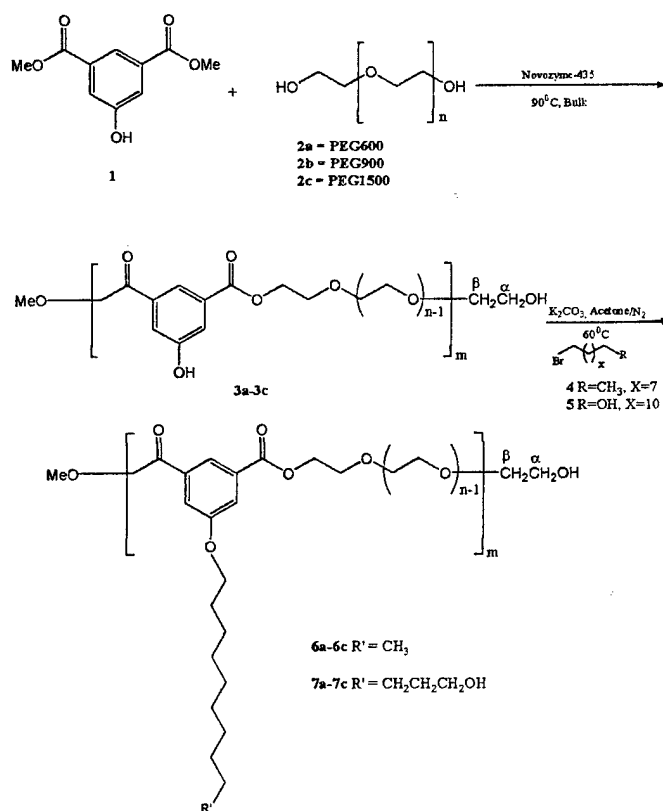
**Figure 3.** Comparison of <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) spectra of a) polyethylene glycol diacid 600 (2); b) 4-hydroxymethylphenol (1); c) pegylated macromer, 3; d) pegylated polymer, 4.

was found that the molecular weight of the polymer obtained decreased with an increase in pH from 4.75 to 10.0. The highest number average molecular weight ( $M_n$ ) 15000 was obtained at pH 4.75 whereas the lowest molecular weight ( $M_n$ ) 2200 was obtained at pH 10.0. Figure 4 shows the UV absorption spectra of the pegylated macromer 3 and polymer 4, with the tailing in the absorption spectra of 4 to 450 nm as compared to 3. This further confirms the presence of extended conjugation and polymer formation. Depegylation of the pegylated polyphenolic 4 was performed at room temperature using aqueous sodium hydroxide solution to give quantitative yields of the light yellow-colored solid 5 ( $M_n$  2500).



**Figure 4.** UV Absorption spectra of pegylated macromer 3, and the pegylated polymer 4

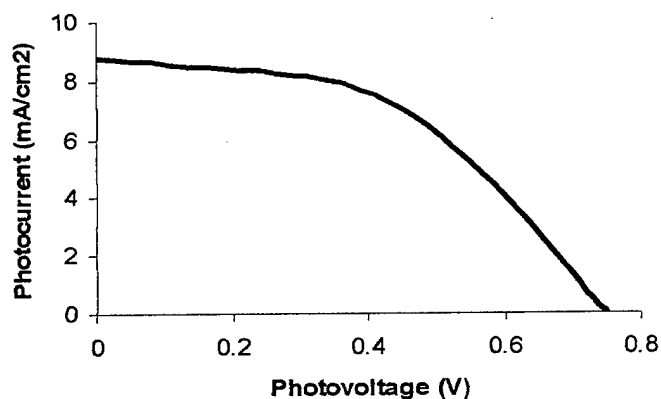
### Scheme 3



Our specific project goal is to develop a gel electrolyte that performs as good as liquid electrolytes presently used for DSSCs. Polyethylene glycol (PEG) is the most commonly used ion-conducting polymer. However, PEGs can undergo crystallization in the presence of salts resulting in reduced mobility of the ions. In order to avoid the crystallization of PEGs and to increase the ionic conductivity, we have designed the synthesis of copolymers containing PEGs (Scheme 3). The condensation copolymerization of dimethyl 5-hydroxyisophthalate with PEGs of varying molecular weights, catalyzed by Novozyme-435 (immobilized *Candida antarctica* lipase B) in bulk was done.

The structure of the resulting polymers Poly[poly(oxyethylene)-oxy-5-hydroxyisophthaloyl] were characterized by  $^1\text{H}$  (1D and 2D) and  $^{13}\text{C}$ -NMR spectroscopic experiments. Further, attaching alkyl chains of different lengths in order to control the microstructure of the polymers has functionalized these polymers. We have also varied the length of the PEG units in the copolymers to tune the amorphous/crystalline properties. The synthesized copolymer **3a** was functionalized by attaching the different alkyl side chains, (with and without functional group at the end of the chain) to phenolic hydroxyl group of the copolymer to give the copolymers, **6a-c** and **7a-c** with long alkyl

chain. The alkylation was done using potassium carbonate in acetone at 60°C. These copolymers **3a**, **6a-c** and **7a-7c** were evaluated for their solar conversion efficiencies. It was found that the copolymer **3a** with PEG600, without any alkyl side chain has showed better efficiency of 3.04% with 8.46mA/cm<sup>2</sup>, 0.74V and 0.488 as short circuit current density, open circuit voltage, fill factors respectively.



**Figure 5.** I-V curve from Novozyme derived Polymer **3a** (PEG 600) based electrolyte incorporated plastic dye-sensitized solar cell

## IMPACT/APPLICATION

The enzymatic synthesis of macromolecular dyes will provide an environmentally benign way for the synthesis of new electronic and photonic active materials. The synthesized pyrene-based macromolecular dyes may be efficient dye sensitizers for the fabrication of photovoltaic cells. The Ruthenium based macromolecular dye is found to be useful as a new class dye sensitizer for the fabrication of TiO<sub>2</sub> photovoltaic cells. The MLCT absorption profile of the polymer complex is seen to extend into visible and near IR region giving rise to possibilities of a novel and versatile class of light harvesting dyes. The considerable efficiency observed in the polymer is encouraging from the view of concept of using biocatalytically synthesized macro dyes in photovoltaic cells.

The promising photoconversion efficiency observed in the ruthenium dinuclear complex synthesized using tpphz is encouraging from the view of concept of using biocatalytically synthesized bridging ligands in photovoltaic dyes. These results open new possibilities towards an alternative, low cost and efficient biocatalytic route to synthesize conjugated aromatic bridging ligands and multinuclear systems for various applications.

We have shown that by combining the selectivities of two different enzymes, novel functionalized materials can be synthesized while circumventing much of the protection/deprotection chemistry. It is anticipated that this approach is not limited to the phenol based reactions and that many other natural or unnatural substrates can be used. It is important to note that lipases and peroxidases are among the most broadly used selective enzymes as they catalyze a tremendous variety of reactions on different substrates. We have synthesized novel Novozyme-435 catalyzed PEG based polyelectrolyte which showed promising efficiency in plastic DSSC. These PEG based gel polyelectrolytes would replace the liquid and ionic liquid electrolytes in DSSCs to overcome several device stability problems.

## **TRANSITIONS**

The results developed during the research will be transitioned or expanded into ONR and other Federal funded programs and collaborations with industrial partners are being pursued. A number of device concepts have been pursued in collaboration with Molecular Technologies Inc. in Westford, presently Konarka Technologies, Lowell, Massachusetts. Konarka Technologies (KTI) was formed in 2001 with the overall goal of developing and commercializing a flexible, low cost, manufacturable solar module based on dye-sensitized titanium oxide ( $\text{TiO}_2$ ). Inexpensive PV modules with a cost of \$0.5/Wp (\$0.05-0.06/KWh) will be competitive with commercial electricity, and will help in deploying cleaner energy producing PV modules for domestic energy needs. The performance, the material/manufacturing cost and increased volume production of the modules are the three key parameters, which will determine the final cost of solar electricity. Konarka Technologies Inc (KTI) has already addressed the later two issues and is targeting improved performance of solar cells. KTI has already achieved over 4 % conversion efficiency in laboratory cells on flexible plastic substrates using standard ruthenium based N3 dye and liquid electrolyte. KTI with UMASS Lowell, is exploring bio-derived macrodyes and quasi-solid electrolytes, in order to reduce the cost of solar modules. KTI has carried out PV characteristic studies on some of the macrodyes and a polyelectrolyte in order to employ them in KTI's devices. Rigorous testing is in progress. Due to its use of low-cost materials and roll-to-roll manufacturing, KTI's technology will make photovoltaics (PV) broadly accessible, and create additional markets for PV that are non-existent today.

## **RELATED PROJECTS**

A US army Natick Laboratories funded project on solar cell is ongoing. The focus of this work is optimization of efficiency and processing of materials. However, the knowledge obtained is applied developing solar cells using macrodyes made using biocatalytic process.

## PUBLICATIONS

1. Singh, A.; Roy, S.; Samuelson, L.A.; Bruno, F.F.; Nagarajan, R.; Kumar, J.; John, V.; Kaplan, D.L. (2001), "Peroxidase, Hematin, and Pegylated-Hematin Catalyzed Vinyl Polymerizations in Water", *Journal of Macromolecular Science*, A38: 1219-1230.
2. Sahoo, S.; Nagarajan, R.; Samuelson, L.; Kumar, J.; Cholli, A.L.; Tripathy, S.K. (2001), "Enzymatically Synthesized Polyaniline in the Presence of a Template Poly(vinylphosphonic Acid): A Solid State NMR Study", *Journal of Macromolecular Science*, A38: 1315-1328.
3. Liu, W.; Lee, S. -H.; Yang, S.; Bian, S.; Li, L.; Samuelson, L.A.; Kumar, J.; Tripathy, S.K. (2001), "Biologically Derived Photoactive Macromolecular Azodyes", *Journal of Macromolecular Science*, A38: 1355-1370.
4. Bruno, F.F.; Nagarajan, R.; Stenhouse, P.; Yang, K.; Kumar, J.; Tripathy, S.K.; Samuelson, L. (2001), "Polymerization of Water-Soluble Conductive Polyphenol Using Horseradish Peroxidase", *Journal of Macromolecular Science*, A38: 1417-1426.
5. Mosurkal, R.; Roy, S.; Kumar, J.; Samuelson, L.A.; Tripathy, S.K. (2002), "Biocatalytic Synthesis of a Ruthenium Macromolecular Complex for Photovoltaics", *Journal of Macromolecular Science*, A39: 1195-1206.
6. Kumar, R.; Shakil, N.A.; Chen, M.-H.; Parmar, V.S.; Samuelson, L.A.; Kumar, J.; Watterson, A.C. (2002), "Chemo-Enzymatic Synthesis and Characterization of Novel Functionalized Amphiphilic Polymers", *Journal of Macromolecular Science*, A39: 1137-1149.
7. Kumar, J.; Liu, W.; Roy, S.; Nagarajan, R.; Tripathy, S.; Bruno, F.; Samuelson, L.A. (2003) "Enzymatic and Biomimetic Synthesis of Electroactive Polymers and Their Optical and Electronic Properties", *International Journal of Plastics Technology*, 6: 32-36.
8. Mosurkal, R.; Kumar, J.; Samuelson, L.A. (2003) "Biocatalytic Synthesis of Conjugated Bridging ligand, tetrapyrrodo[3,2-a:2',3'-c:3",2"-h:2"',3'''-j]phenazine (tpphz) and a Dinuclear Ruthenium Complex", *Inorganic Chemistry*, 42, 5450.
9. Mosurkal, R.; Kumar, R.; Bruno, F.F.; Nagarajan, R.; Samuelson, L.; Kumar, J. (2004), "Biocatalytic synthesis of novel electronic and photovoltaic materials", *Proceedings of IUPAC symposium* (submitted).
10. Kumar, R.; Bruno, F.F.; Parmar, V.S.; Kumar, J.; Watterson, A.C.; Chittibabu, K.G.; Samuelson, L.A. (2004), "'Green'-enzymatic synthesis of pegylated phenolic macromer and polymer", *Chemical Communications*, 862.